Docket No.: 606952000420

App No.: 10/812,156 Docket No.: 6069
Inventor: Robert A. VUKOVICH et al.
Title: PREPARATION OF METAL MESOPORPHYRIN
COMPOUNDS

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Nomenclature of Tetrapyrroles

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Appendix 2

Comparison of the Numbering of the Trivially Named Porphyrins(TNP) with Numbering Based on CNOC/CAS

20	ı.	•	•	•	•	•	•	ı	ı	ı	ı	•		•
18	Cet	B	Me	Cet	茁	Me	Me	茁	Me	茁	Me	茁	-CHO	Cet
17	Cm	Cet	Cet	Me	Me	超	茁	Me	茁	Me	茁	Me	Cet	-CHO
15	1	•	٠	•	•	•	ı	ı	•	•		•	ı	ı
13	Cet	CB	Cet	Me	Ēţ	Me	Εţ	Me	Εţ	Me	Me	亞	Cet	Me
. 12	Cm	Cet	Me	Cet	Me	亞	Me	Et	Me	Ēŧ	Et	Me	Me	R'CH(OH)-
∞	Cet	Cm	Me	Cet	Ēţ	Me	Me	Ēţ	西	Me	Et	Me	Vn	Me
7	Cm	Cet	Cet	Me	Me	Ēţ	古	Me	Me	Et	Me	Ē	Me	Vn
	Cet												_	
8	Cm	Cet	Me	Cet	Me	豆	Me	Ē	Me	Ē	Me	Œ	Me	Cet
Numbering 2 Basis	TNP	CNOC/CAS	INP	CNOC/CAS	TNP	CNOC/CAS	TNP	CNOC/CAS	TNP	CNOC/CAS	TNP	CNOC/CAS	TNP	CNOC/CAS
TNP Trivial Name Numbering Basis	1. Uroporphyrin I		2. Coproporphyrin II		3. Etioporphyrin I		4. Etioporphyrin II		5. Etioporphyrin III		6. Etioporphyrin IV		7. Cytoporphyrin	

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8. Protoporphyrin	TNP Me CNOC/CAS Cet		Vn Me	Me Vn	V _n Me	Me Vn	Cet Me	1 1	Cet Me	Me Cet	1 1	
9. Mesoporphyrin	TNP Me CNOC/CAS Cet		Et Me	Me Et	Et Me	Me Et	Cet Me	1 1	Cet Me	Me Cet	1 1	
10. Hematoporphyrin	TNP Me CNOC/CAS Cet	\circ	H ₃ CH(OH)- Me	Ме СН ₃ СН(ОН)-	CH ₃ CH(OH)- Me	Me CH ₃ CH(OH)-	Cet Me	1 1	Cet Me	Me Cet	1 1	
11. Deuteroporphyrin	TNP Me		Me -	Me Me		Me Me	Cet	1 1	Cet Me	Me Cet	1 1	
12. Rhodoporphyrin	TNP Me CNOC/CAS Cet		Et Me	Me Me	西西	Me Me	-соон Et	1 1	Cet Me	Ме -СООН	1 1	
13. Pyrroporphyrin	TNP Me CNOC/CAS Cet		Et Me	Me Me	西西	Me Me	· 亞	1 1	Cet Me	Me -		
14. Phylloporphyrin	TNP Me CNOC/CAS Cet		Et Me	Me Me	西西	Me Me	- 描	Me .	Cet Me	Me -	Me	

R¹=

 $Cm = -CH_2COOH$

 $Cet = -CH_2CH_2COOH$

CNOC = IUPAC Commission on Nomenclature of Organic Chemistry

CAS = Chemical Abstracts Service

Note: Cet and Cm are often abbreviated to P and A. This is acceptable provided these are defined as CH2CH2CO2H and CH₂CO₂H respectively.

Appendix 3

Fischer trivial names

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Principles. Cm = -CH2COOH; Cet = -CH2CH2COOH; CNOC = IUPAC Commission on the Nomenclature of Organic Chemistry; CAS

12 13 17 18 Numbering Substituents and Locants

Fischer scheme. The Roman numerals here do not mean the same as those employed in the trivial names in Table 3. Both systems are referred

to as "type numbering". The start point and sequence of locant numbering used by Fischer are retained (although the locant numbers follow

Comparison of the Numbering of the Fischer Trivially Named Porphyrins (TNP) with Numbering Based on CNOC/CAS Numbering

The names all carry a Roman numeral. The name without such a numeral is already defined in Table 2, and corresponds to isomer IX in the

The names are illustrated for isomers of mesoporphyrin, but may also be used for deuteroporphyrin (for Et read H), haematoporphyrin (for Et

read -CH(OH)CH₃) and protoporphyrin (for Et read -CH=CH₂).

A. Porphyrins

The following extensions to the list of accepted trivial names are proposed as permitted: they encompass a further selection of trivial names

due to Hans Fischer. They each refer to a single compound and must not be used as a basis for semisystematic nomenclature.

Isomer Type Basis Number

Fischer

Chemical Abstracts Service.

the 1-24 system, TP-1.2).

Me Et Me Et Me Cet Me Cet

CNOC/CAS Cet Me Cet Me Et Me Et Me Me Cet Me Et Me Cet Me Et

CNOC/CAS Cet Me Et Me Cet Me Et Me

TNP Me Et Et Me Me Cet Cet Me CNOC/CAS Cet Me Me Et Et Me Me Cet

Me Cet Et Me Me Et Cet Me CNOC/CAS Cet Me Me Cet Et Me Me Et INP

 \geq

 \equiv

TNP Me Cet Me Cet Me Et Et Me CNOC/CAS Cet Me Cet Me Me Et Et Me Me Cet Et Me Me Cet Et Me CNOC/CAS Cet Me Me Et Cet Me Me Et Z

III

TNP Me Cet Me Et Me Cet Et Me CNOC/CAS Cet Me Et Me Cet Me Me Et

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VIII	TNP	Me Et Me Cet Me Cet Et Me	Me	Cet	Je C	et E	Σ̈́	
	CNOC/CAS Cet Me Cet Me Et Me Me Et	Cet Me	Çe	Me E	∠ ;;	le M	e Et	
XI	TNP Me Et Me Et Me Cet Cet Me CNOC/CAS Cet Me Et Me Et Me Me Cet	Me Et Cet Me	₩ Et	Et N Me E	7 e C	et C	et Me Te Ce	
×	TNP Me Et Me Cet Me Et Cet Me CNOC/CAS Cet Me Et Me Me Cet Et Me	Me Et Cet Me	Me Et	Cet N Me N	he E	it et E	et Me	
IX	TNP Me Cet Me Et Me Et Cet Me CNOC/CAS Cet Me Me Cet Et Me Et Me	Me Cet Cet Me	Me	Et N Cet E	de E	te C	et Me	
IIX	TNP Me Et Et Me Cet Me Me Cet Cet CNOC/CAS Cet Me Me Cet Me Et Et Me	Me Et Cet Me	Et Me	Me Cet N	et N	de ₹	e Ce	. .
XIII	TNP Et Me Me Et Me Cet Cet Me CNOC/CAS Cet Me Et Me Me Et Me Cet	Et Me Cet Me	₩ Et	Et N Me N	de C	set C	et Me Fe Ce	. ب
ΛΙΧ	TNP Me Cet Et Me Et Me CNOC/CAS Cet Me Cet Me Me Et	Me Cet Et Me Et Me Me Cet Cet Me Cet Me Et Me Et	Cet Cet	Me E Me	it N de E	de X	Me Cel Me Et	٠.
XX	TNP Me Cet Et CNOC/CAS Cet Me Et	Me Cet Et Me Cet Me Me Et Cet Me Et Me Me Et Me Me Cet Et Me	西西	Me N	Set N	de Nei	le Et t Me	4

COAH

Thus mesoporphyrin VI is

B. Bilindiones

structure (tabulated above) which has been formally broken at the meso bridge denoted by the Greek letter (Fischer numeration, Fig. 1). The The following Fischer trivial names for bile pigments are permitted. Each refers to a single compound, and must not be used as the basis for semisystematic nomenclature. They each have a Roman numeral and a Greek letter as suffixes: the Roman numeral refers to the porphyrin structures and names have already been referred to in TP-6.3 and TP-6.4 and are: App No.: 10/812,156

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The names without a Roman numeral and Greek letter are already defined in $\overline{\text{Fig. 16-22}}$: in each case the IX α isomer is implied. For convenience the structures of the biliverdin isomers mentioned in the previous paragraph are tabulated below.

biliverdin III α , biliverdin IX α (= biliverdin), biliverdin IX β , biliverdin IX γ , biliverdin IX δ , biliverdin XIII α , together with the corresponding

hydrogenated derivatives (e.g. bilirubins, mesobiliverdins).

TP appendix 2 and 3

Me Vn Me Vn Me Cet Cet Me Cet Me Me Vn Me Vn Me Cet Me Vn Me Cet Cet Me Vn Me Me Cet Cet Me Me Vn Me Vn Vn Me Me Cet Cet Me Me Vn Me Vn Me Cet Cet Me Me Vn 12 13 17 18 Substituents at Positions **∞** Roman Numeral Designation XIIIα ΙΠα ΙΧα IXβ IXδ IX_{γ}

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come upon one such trend in Chapter 10: the general tendency for ionization energy to increase along any row of the periodic table. Our discussion in this and subsequent chapters will reveal other similar horizontal trends in chemical and physical properties. In addition, important diagonal relationships appear: There are often similarities between an element and its diagonal neighbor in the succeeding column and row of the periodic table. To make the existence of such relationships clear, and to emphasize the usefulness of the periodic table, in the remainder of this chapter we shall discuss some of the clearer trends in the properties of the elements and of some of their common compounds.

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13.2 PERIODIC PROPERTIES

A very large number of chemical and physical properties of the elements vary periodically with atomic number. Some of these properties are related to the electron configurations of the atoms in quite obscure and complicated ways, while others are more susceptible to interpretation and explanation. These latter properties, such as electrical conductivity, crystal structure, ionization energy, electron affinity, possible oxidation states, and atomic size, are related to each other and to the general chemical behavior of the elements. Thus an appreciation of the importance of these particular properties, and of how they vary throughout the periodic table, will help us to correlate, remember, and predict the detailed chemistry of the elements.

Electrical and Structural Properties

The chemical elements can be classified as metals, nonmetals, and semimetals on the basis of their electrical properties alone. Metals are good conductors of electricity, and their electrical conductivity decreases slowly as temperature is increased. The nonmetals are electrical insulators: Their ability to conduct electricity is either extremely small or undetectable. The electrical conductivities of semimetals or semiconductors are small but measurable, and tend to increase as temperature increases. Electrical conductivities are usually measured in units of ohm⁻¹ · cm⁻¹, and a conductivity of 1 ohm⁻¹ · cm⁻¹ means that if a potential difference of 1 volt is applied to opposite faces of a 1-cm cube of material, a current of 1 amp will flow. The electrical conductivities of metals are, in general, greater than approximately 1×10^4 ohm⁻¹ · cm⁻¹, as Table 13.2 shows. The shaded group of semimetals have small conductivities (in the range from 10 to 10^{-5} ohm⁻¹ · cm⁻¹) that are sensitive to impurities, and nonmetals have even smaller conductivities (i.e., are insulators).

Table 13.2 shows that the metallic elements appear in the left-hand part of the periodic table, and are separated from the nonmetals by a diagonal band of semimetals that runs from boron to tellurium. The classification of elements close to this group of semimetals is not always straightforward, for several of the elements of groups IVA, VA, and VIA occur in different allotropic forms,

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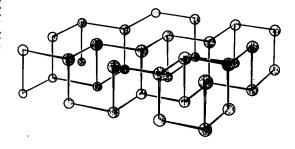
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Table 13.2 The electrical conductivities of the elements in units of 10⁴ ohms⁻¹ · cm⁻¹

Li 11.8	Be 18		С	N.	Ó,	F
Na 23	Mg 25	AI 40		Р	ŝ	CI
K 15.9	Ca 23	Ga 2.4			Se	Br
Rb 8.6	Sr 3.3	In 12	Sn 10	Sb 2.8		1
Cs 5.6	Ba 1.7	TI 7.1	Pb 5.2	Bi 1.0	Ро	At

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Ըս	Zn.
—	1.2	0.6	6.5	20	11.2	16	16	65	18
Y .	Zr 2.4	Nb —	Mo 23	Tc —	Ru 8.5	Rh 22	Pd 1	Ag :	Cd 15
La	Hf	Ta	W	Re	Os	lr	Pt	° Au	Hg
1.7	3.4	7.2	20		11	20.	- 10	49	4.4

each of which has different electrical properties. For example, the α -phase of tin, sometimes called grey tin, has the diamond type of crystal lattice found in silicon and germanium, and like these elements, grey tin has the electrical properties of a semimetal. On the other hand, white tin, the β -phase that is stable above 13°C, is a metallic conductor. As another example, white phosphorus, a molecular solid of P_4 units, and red phosphorus, which has a complex chain structure, are both electrical insulators and thus are of nonmetallic character. In contrast, the allotrope black phosphorus has a crystal structure made up of corrugated sheets, as shown in Fig. 13.2, and in this form phosphorus behaves like a semimetal. Similar phenomena are found for selenium.



The crystal structure of the black phosphorus allotrope.

FIG. 13.2